High resolution spectroscopy of ammonia in a hollow-core fiber

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Abstract: We have demonstrated frequency modulation saturation spectroscopy of the $\nu_1 + \nu_3$ band of ammonia in hollow-core photonic bandgap fibers (HC–PBFs). Previously blended lines have been resolved and the corresponding molecular transitions assigned. Cross–over resonances are observed between transitions that do not share a common level. We have measured the pressure dependence of the line shape and determined the collisional self–broadening coefficients for ammonia. The many absorption lines of ammonia in the 1.5 μm wavelength region are potential frequency references lines for optical communication as well as candidates for spectroscopic trace gas monitoring.

OCIS codes: (060.5295) Photonic crystal fibers; (300.6460) Saturation Spectroscopy; (060.2630) Frequency modulation.

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1. Introduction

Hollow-Core Photonic Bandgap Fibers (HC-PBFs) [1] allow the confinement of high intensity light over long absorption paths. In this way, saturated absorption spectroscopy can be performed in these fibers [2–5]. When combined with frequency-modulation (FM) spectroscopy, high sensitivities in the detection of weak molecular transitions can be achieved [6]. In this paper, we report the observation of FM saturation spectroscopy on selected absorption lines in the near-infrared $\nu_1 + \nu_3$ band of ammonia ($^{14}NH_3$) in a HC-PBF. To the best of our knowledge, this is the first observation of sub-Doppler spectroscopy of ammonia in the near-infrared.

The main aim of the work is to demonstrate that the HC-PBF is a useful tool in high-resolution spectroscopy. Previous experiments on saturation spectroscopy in HC-PBFs have focused on acetylene in the 1.5 μm range [2–5]. However, saturated absorption of acetylene has also been observed in both enhancement cavities [7] as well as in conventional gas cells using moderate laser power [8]. In this work we show that high resolution and high signal-to-noise ratio can easily be obtained for the ammonia lines, which are about 50–100 times weaker than the acetylene lines. We also demonstrate that sub–Doppler spectroscopy can assist in resolving blended lines, of which there are many as noted in references [9] and [10], and thus contribute to further transition assignments. Finally, we have observed crossover resonances between pairs of transitions that do not share a common level. This is a rather unusual phenomenon, and we argue that these are due to predominantly collisional transitions. The ammonia lines may be useful as wavelength references in the 1.5 μm region. Acetylene has been the main choice of reference gas so far, but even including isotopic species there is a limited wavelength coverage and ammonia is a potential candidate for references above 1550 nm. Furthermore, better knowledge of the ammonia spectrum in the 1.5 μm range is desirable for spectroscopic trace gas monitoring of ammonia [11].

2. Experimental setup

Our experimental setup is quite similar to the configuration used for optical heterodyne saturation spectroscopy in Ref. [12] except for the replacement of the conventional gas cell with a gas-filled HC-PBF. A detailed sketch of the setup is shown in Fig. 1. Compared with the pre-

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viously used setup [5] an electro–optic modulator (EOM, Uniphase UTP Model PM 150) has been added and the lenses used for focussing the beams into the HC–PBF have been moved inside the vacuum chamber. Briefly, the optical beam from an external cavity diode laser (ECL) is split and amplified by two 60 mW erbium doped fiber amplifiers (EDFAs). The linewidth of the laser is below 1 MHz. A Fabry-Perot (FP) resonator and a wavelength meter are used to provide the frequency scale and the wavelength reference for the ECL, respectively. The output of the EDFA providing the pump beam is amplitude modulated at 91 kHz by a 40 MHz acousto-optical modulator (AOM). The output of the EDFA providing the probe beam is phase-modulated by an electro-optic modulator (EOM) at a frequency of 54 MHz. The pump and the probe beam are coupled into free-space by lens L1 (red beam) and lens L4 (green beam), respectively. Neutral density filters and wave plates are used to adjust the polarization and power of the pump and probe beams. The beams are transmitted through angled windows into the vacuum chamber and coupled into the HC-PBF by lenses L2 and L3. A 3.5 m long HC-PBF produced by Crystal Fibre Ltd. (type HC19-1550-01 with 20-μm diameter core) was used. Only about 20 cm of each fiber end are placed inside the vacuum chamber, the rest is placed on the optical table outside. Apiezon vacuum sealing is used to seal the 0.3 mm holes through which the fiber is inserted. After evacuation, the chamber is filled with ammonia which then diffuses into the fibre. An optical isolator (OI) is used to minimize feedback from the pump. A polarizing beamsplitter (PBS) reflects the probe onto a fast photodetector (PD, New Focus Model 1811). The signal is recovered by phase-sensitive detection using a radio frequency mixer (MIX) and a lock-in amplifier (LI). Approximately 68% of the pump power and 62% of the probe power were transmitted through the evacuated fiber.

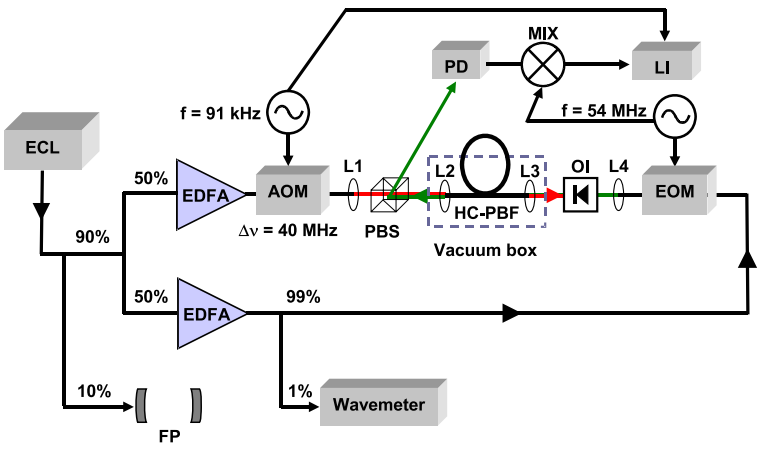

Fig. 1. Experimental setup for FM saturation spectroscopy in a HC–PBF.

3. Results

The spectrum of ammonia in the 1.5 μm region is very dense [9]. In the wavelength range accessible by our set-up, saturated absorption could be observed on very many transitions with absorption strength larger that 1.5×10^{-4} cm^{-1} Torr^{-1}. The focus of this paper is not to map the entire spectrum of ammonia at sub-Doppler resolution in this wavelength region, but rather to demonstrate the feasibility of high-resolution spectroscopy of ammonia in HC-PBFs. Therefore, we have selected a few lines in order to demonstrate the types of spectroscopic features that can be expected. The *s* and *a* components of five different *(J,K)* levels near each other

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were chosen and listed in Table 1. In the present work the wavelengths were measured using a Burleigh wavemeter, which was calibrated against a well known transition in acetylene

Table 1. Selected lines observed by FM saturation spectroscopy

Wavenumber[a] (cm^{-1})	Corresponding wavelength (nm)	Absorption strength[b]	Line assignments[c]	Measured wavelength (nm)	Assignments[d]
6553.140	1525.986	3.0988	${}^{P}P(3,1)a$	1525.9825	a
(b)			${}^{P}P(3,1)s$	1525.9862	s
6548.792	1526.999	5.7100	${}^{P}P(4,3)a$	1526.9975	
6548.608	1527.042	5.9469	${}^{P}P(4,3)s$	1527.0414	
6541.388	1528.727	3.9703	${}^{P}P(4,2)a$	1528.7237	a
(b)			${}^{P}P(4,2)s$	1528.7278	s
6529.184	1531.585	4.6082	${}^{P}P(5,3)s$	1531.5835	
6528.894	1531.653	4.4665		1531.6513	${}^{P}P(6,6)s$
6528.764	1531.683	7.6332	${}^{P}P(5,3)a$	1531.6815	${}^{P}P(6,6)a$
				1531.6824	${}^{P}P(5,3)a$

[a] Wavenumbers are from Ref. [9]

[b] Absorption strength from Ref. [9], in units of $10^{-4}cm^{-1}$/Torr

[c] Line assignments are from Ref. [9], (b) indicates that the two lines were reported as blended lines

[d] The full assignments are from references [10] and [13]. The *s* and *a* assignments are from this work (see text)

Examples of observed FM saturation signals are shown in Figs. 2, 3 and 4. Each signal is the result of about 10 seconds of averaging. The observed spectra have been fitted to the following equation valid for small phase modulation index and at low saturation [12]:

$$I_{FM}(\nu) = \alpha[(L^- - L^+)\sin\varphi + (D^+ - 2D^* + D^-)\cos\varphi] \tag{1}$$

Where α is a scaling factor, φ is the phase shift between the local oscillator and the mixer and L^j and D^j are profile functions defined as follows:

$$L^j = \frac{\Gamma^2}{\Gamma^2 + (\nu^j - \nu_0)^2} \tag{2}$$

and

$$D^j = \frac{\Gamma(\nu^j - \nu_0)}{\Gamma^2 + (\nu^j - \nu_0)^2} \tag{3}$$

Here ν is the laser frequency and ν_0 is the frequency of the resonance center shifted by $\frac{1}{2}\Delta\nu$ where $\Delta\nu$=40 MHz is the AOM frequency shift of the pump. The superscript j can have three values, $j = +, *, -$, and the corresponding frequencies are $\nu^{\pm} = \nu \pm \frac{f_m}{2}$ and $\nu^* = \nu$, where f_m is the phase modulation frequency. Γ is the linewidth (HWHM) of the resonance. The fit to a single line has essentially four free parameters, α, φ, Γ, and ν_0. The fits are inserted in the upper parts of Figs. 2, 3, and 4 as red solid lines, the experimental data are shown as blue dots, and the residuals of the fits are shown in the lower parts. As can be seen, an excellent agreement between the theoretical lineshape and the experimental data is demonstrated in all three cases.

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The linewidths deduced from the shown spectra have contributions from both self-pressure broadening and wall collisions as discussed further below.

The line shown in Fig. 2 is the ${}^{P}P(4,3)a$ transition of the $\nu_1+\nu_3$ band at 1526.9975 nm. There is clearly only one visible absorption line. The linewidth (HWHM) from the fit is 29 MHz, which is approximately 9 times narrower than the Doppler broadened line. Similarly, only one line was observed at 1527.0414 nm, 1531.5835 nm and 1531.6513 nm, respectively, all with approximately the same linewidth.

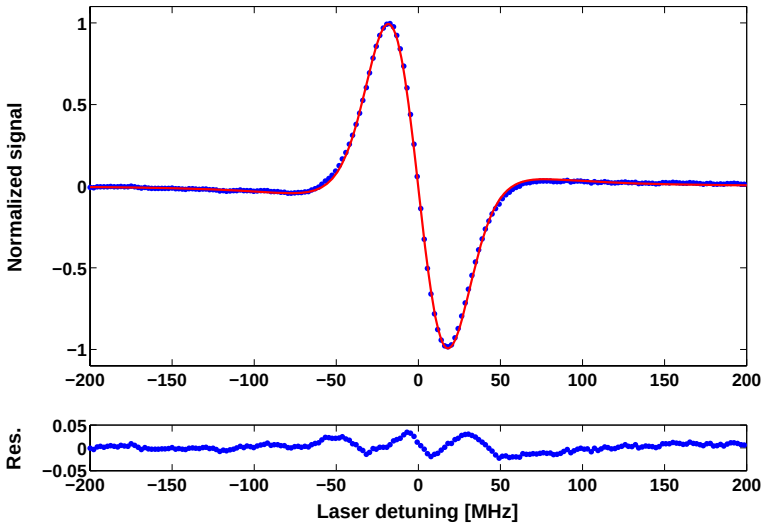

Fig. 2. FM saturation signals of $^{14}NH_3$ in a 3.5-m HC-PBF at a pressure of 2 hPa. The line corresponds to the ${}^{P}P(4,3)a$ transition at 1526.9975 nm. Blue dots represent the measured signal and solid red line the fit. The residual is shown in the bottom panel.

Two cases that where previously reported as blended lines [9] have been resolved in the present work. In addition, we have resolved a third doublet (1531.6815 nm and 1531.6824 nm), which has not previously been suggested as a blended line. The lines at 1531.6815 nm and 1531.6824 nm shown in Fig. 3 are the ${}^{P}P(6,6)a$ and ${}^{P}P(5,3)a$ transitions, respectively, in the $\nu_1+\nu_3$ band [13]. The linewidths (HWHM) of the two transitions are 26 and 30 MHz, respectively, at a pressure of 2 hPa. In this particular case accidental overlap between two lines with different (J,K) values were resolved. A more common situation is the overlap between two transitions having the same (J,K) but different inversion symmetry. As an example the energy level diagram and the corresponding allowed transitions are shown in Fig. 5 for the levels involving ${}^{P}P(4,2)$. The observed sub–Doppler spectrum of the resolved ${}^{P}P(4,2)$ lines is shown in Fig. 4. In saturation spectroscopy the presence of multiple levels can result in crossover resonances. Crossover resonances have been extensively reported in the literature particularly within atomic and diatomic saturation spectroscopy, while there are fewer reports where polyatomic molecules are involved and usually these involve hyperfine structure or Zeeman/Stark split levels. Examples of polyatomic molecules where crossover resonances have been observed are methane [14], ammonia [15], and osmium tetroxide [16]. These resonances occur when the laser is tuned exactly midway between two transitions, so that for some velocity group the pump drives one transition while the probe drives another. However, the absorption or dispersion of the probe is only influenced by the presence of the pump if the two transitions are somehow coupled. Therefore, crossover resonances in saturation spectroscopy are usually observed when the two transitions share a common upper or lower level. Only a few examples of crossover

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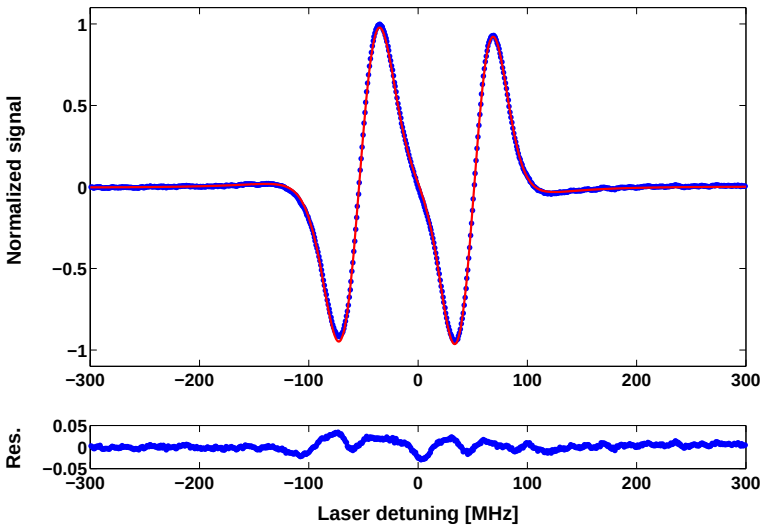

Fig. 3. FM saturation signals of $^{14}NH_3$ in a 3.5-m HC-PBF at a pressure of 2 hPa. The lines correspond to the $^PP(6,6)a$ and $^PP(5,3)a$ transitions at 1531.6815 nm and 1531.6824 nm, respectively.

resonances in atomic four-level systems have been observed, e.g. by radiative coupling of two levels [17]. For the two transitions with different inversion symmetry shown in Fig. 4 we do indeed observe a small crossover resonance with a frequency that is the average of the two regular absorption lines. A similar spectrum was observed for the two lines of the $^PP(3,1)$ transition. This is to our knowledge the first report of crossover resonances in a molecular four-level system. We argue that collisional transfer between close-lying *a* and *s* states with the same (J,K) is responsible for the required coupling in order to observe the crossover resonance in a four-level system. This observation may be useful in connection with spectroscopic assignments as no crossover resonances are observed in the case of blended transitions corresponding to different (J,K), as seen in Fig. 3.

For the three FM signals shown in Fig. 4 we have investigated the pressure dependence of the signal amplitude and the signal linewidth. The amplitudes and linewidths were obtained from fits at ten different pressure values. Due to adsorption of ammonia on the inner wall of the fiber, it takes quite a long time to reach pressure equilibrium when reducing the pressure from high to low in the vacuum chamber. Thus, we use the resonant absorbance to deduce the average ammonia pressure in the fiber rather than the actual reading from the pressure gauge. For the linewidth data we have averaged the data for the three lines at each pressure as the differences between the lines were within the measurement uncertainty. The results are shown in Figs. 6 and 7.

From the results shown in Fig. 7, the average pressure broadening coefficients, γ_{NH_3}, for the three lines are determined to be (11.6 $\pm$ 0.7) MHz/hPa. The uncertainty is given as the standard uncertainty from the fit. The extrapolation to 0 Pa gives the linewidth due to mainly wall collisions (or, equivalently, transit time broadening). We find that the HWHM transit time broadening is (19 $\pm$ 1) MHz. The theoretical value is $\Delta\nu = 0.444u/L$=13.4 MHz, where $u = \sqrt{8kT/\pi M} = 605$ m/s is the mean molecular velocity and L is the 20 μm core diameter.

From the pressure dependence data we calculate the ratio between the crossover signal amplitude and the amplitude of the low wavelength signal. The result is shown in Fig. 8. There is a clear relative increase in the crossover resonance compared with the regular signals at higher

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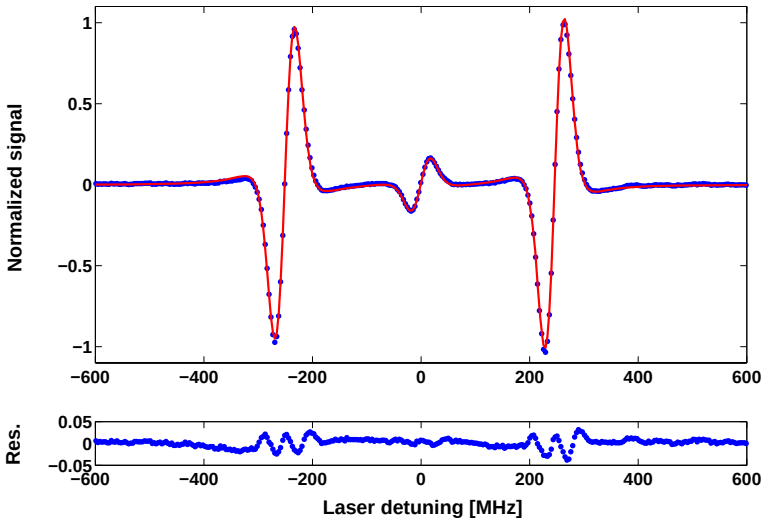

Fig. 4. Saturated absorption signals of the ${}^{P}P(4,2)s$ and ${}^{P}P(4,2)a$ absorption lines at 1528.7237 nm and 1528.7278 nm, respectively. A cross-over resonance is observed between the two lines. The pressure used was 63 Pa

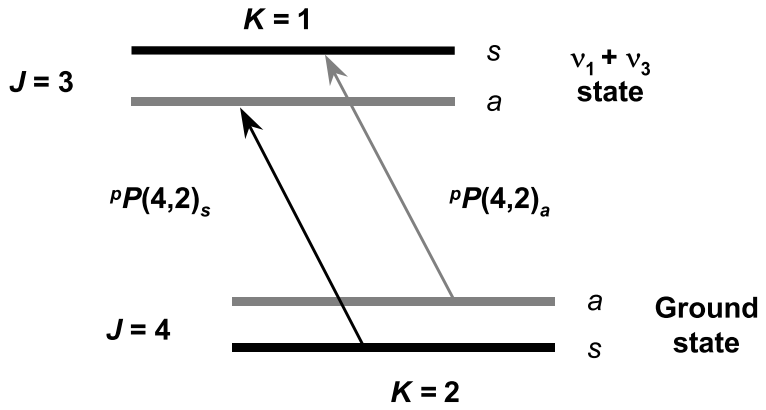

Fig. 5. Energy level diagram of ammonia including the ${}^{P}P(4,2)s$ and ${}^{P}P(4,2)a$ transitions at 1528.7278 nm and 1528.7237 nm. The ground state inversion is 0.7235628 cm^{-1}

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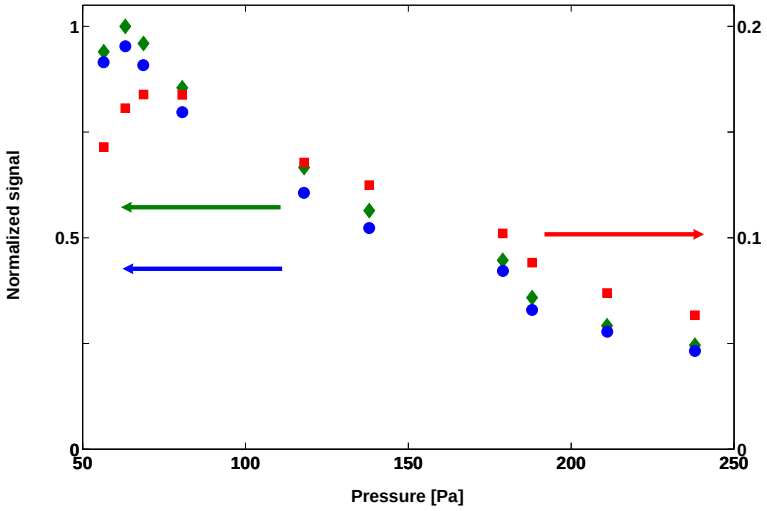

Fig. 6. Normalized amplitudes of the FM saturated signals as a function of pressure. The measurement results for the 1528.7278 nm line is indicated with green diamonds (left scale), for the 1528.7237 nm line with blue circles (left scale) and for the crossover resonance with red squares (right scale).

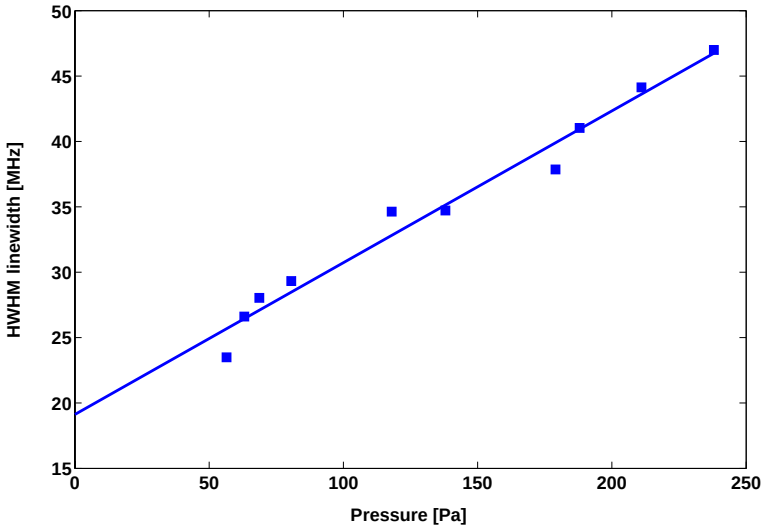

Fig. 7. Average HWHM linewidth of the resonances shown in Fig. 4 as a function of pressure. The solid line is the corresponding linear fit.

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pressure. As the pressure increases the collision relaxation and thereby the coupling of the two transitions will increase and thus the crossover signal gains in strength compared with the signals due to the normal transitions. The fact that the crossover to line ratio does not go to zero at zero pressure can be explained by wall collisions.

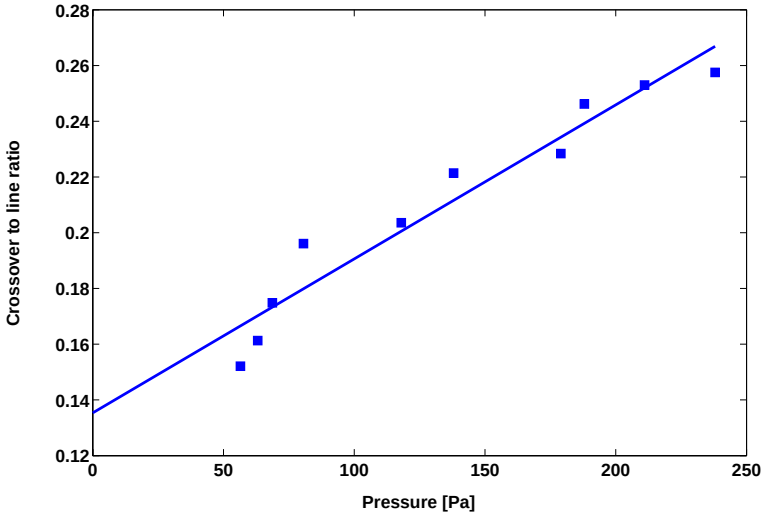

Fig. 8. Ratio between the crossover signal and the signal at 1528.7237 nm as a function of pressure. The line is a linear fit to the measured data.

4. Discussions and assignments

In previously reported work [5] we showed that the line broadening due to wall collisions could be reduced by a factor 3 when selecting the slow moving molecules in acetylene in a HC–PBF. In order to observe this line narrowing low pressure has to be used. However, due to the much weaker absorption cross–section of ammonia compared with acetylene a much longer fiber has to be used. Such a fiber was not available and thus significant line narrowing was not observed in this work.

Optical telecom lasers are relatively inexpensive and therefore attractive for use in trace gas monitoring. Webber et. al. [11] suggested six ammonia spectral features that could be used for trace ammonia detection in air-quality and combustion emissions-monitoring, including the spectral features around 6528 cm^{-1} (1531.6 nm) containing six observed lines. They discussed differences between their observations and those of Ref. [9] and observed a large discrepancy in line strength for the line at 6528.76 cm^{-1}. As noted above this is not a single line but consist of the the ${}^{P}P(6,6)a$ and ${}^{P}P(5,3)a$ transitions. Therefore, it is interesting that the calculated spectrum in Ref. [11] fit so well with the strength of their observed spectrum. With respect to the other lines in the feature there were several that was observed in the Fourier transform spectrum by [9], which was not observed in the laser absorption spectrum by [11]. The lines not observed by Ref. [11] were not observed in the present work either. However, since they are 10–20 times weaker, the reason may be that they could not be saturated.

The assignments of four lines around 1531.6 nm are shown in Table 1. The initial assignments from Ref. [9] are also listed. In a later paper [10] it was suggested that the *a* and *s* components of the ${}^{P}P(6,6)$ transition were blended at 1531.653 nm. Our work indicates that there is only one line under the Doppler broadened absorption at this frequency while, as shown in Fig. 3, there are two lines present at 1531.682 nm. Therefore, one of the ${}^{P}P(6,6)$ components is assigned to

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one of the two transitions observed in Fig. 3 [13].

Ground state inversion transitions involving the (4,2) and (3,1) ground state levels [18] together with the previously published assignments and transition frequencies involving infrared transitions to the excited (3,1) and (2,0) levels [9] allows for assignments of the *s* and *a* components of the ${}^{P}P(4,2)$ and ${}^{P}P(3,1)$ transitions. The assignments are shown in Table 1. We estimate the inversion transition in the excited states a(3,1) and (2,0) to be approximately 22.22 and 22.71 GHz, respectively. Since we have demonstrated that the optical transition can be saturated one should be able to observe infrared microwave double resonance spectra and thus obtain more accurate frequencies of the inversion transitions in the excited state [19]

The values obtained for the pressure broadening coefficients of the lines ${}^{P}P(4,2)s$ and ${}^{P}P(4,2)a$ are in agreement with previously reported values. Gibb et. al. [20] reported values for six lines in the same band, four of these were assigned to the transitions ${}^{R}Q(4,1)a$, ${}^{Q}P(10,6)s$, ${}^{R}Q(5,1)s$, and ${}^{R}Q(5,1)$a. The values for γ_{NH_3} were in the range 8.2 - 17.7 MHz/hPa while Modugno and et. al. [21] found a value of 14.8 MHz/hPa for the ${}^{P}P(7,3)s$ transition and 15.4 MHz/hPa for the ${}^{R}P(6,0)$a transition. In the two references it has been shown that the self-broadening in ammonia is greatly *(J,K)* dependent. It should be emphasized that our pressure broadening coefficients measurements were obtained from Doppler free signals in the pressure range 10 – 200 Pa while those of the above mentioned authors were obtained from Doppler and pressure broadened spectra in the pressure range 50 – 1000 hPa. There are cases reported for the CO molecule [22] and the CO_2 molecule [23] were the pressure broadening coefficients are larger, by up to a factor 4, at low pressures compared with high pressures.

5. Conclusions

We have reported, what to the best of our knowledge, is the first observation of saturation spectroscopy in the $\nu_1 + \nu_3$ band of ${}^{14}NH_3$ in a HC-PBF. The very good signal to noise ratio of the signals will allow the extensive number of absorption lines from ammonia in this wavelength region to be used as wavelength references. The sub-Doppler spectroscopy has been used to resolve previously blended lines [9], thereby, demonstrating that the technique has considerable potential for contributing to unravel the complex spectrum of ammonia in this wavelength region. Crossover signals have been observed between pairs of transitions that do not share a common level. We argue that the transitions are coupled due to collisional transfer between close-lying states. Finally, we have obtained pressure broadening coefficients in good agreement with previously reported values obtained at much higher pressures.

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